

BECKTON ENVIRONMENTAL
LABORATORIES, INC.

SOP NUMBER: 703-012

TITLE:

pH
Electrometric Method
Standard Method 4500 H⁺ B

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pH (Electrometric Method)
SM 4500-H⁺ B

1.0 Scope and Application

- 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

2.0 Summary of the Method

- 2.1 The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a glass electrode with a reference electrode or a combination electrode.

3.0 Detection Limit

- 3.1 N/A

4.0 Definitions

- 4.1 The following general terms are defined for use in this document or where applied:
- pH:** is defined by Sorenson is $-\log [H^+]$; it is the 'intensity' factor of acidity.
- Buffer:** is the amount of strong acid or base, usually expressed in moles per liter, needed to change the pH value of 1 liter sample by unit.
- Accuracy:** The closeness of agreement between an observed value and an accepted reference value.
- Batch:** A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit.
- Bias:** The deviation due to matrix effects of the measured value ($x_s - x_u$) from a known spiked amount.
- Control Sample:** A QC sample introduced into a process to monitor the performance of the system.
- Data Validation:** The process of evaluating the available data against the project DQOs to make sure that the objectives are met. Data validation may be very rigorous, or cursory, depending on project DQOs. The available data reviewed will include analytical results, field QC data and lab QC data, and may also include

field records.

Field Duplicates: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

Laboratory Control Sample: A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.

Matrix: The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

Matrix Duplicate: An intralaboratory split sample which is used to document the precision of a method in a given sample matrix.

Precision: The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100 S / \bar{x},$$

where:

\bar{x} = the arithmetic mean of the x_i measurements, and

S = variance; and the relative percent difference (RPD) when only two samples are available.

$$RPD = 100 [(x_1 - x_2) / \{(x_1 + x_2) / 2\}].$$

Reagent Grade: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

Reagent Water: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

5.0 Interferences

- 5.1 The glass electrode is relatively free from interference from color, turbidity, colloidal matter, oxidants, reductants or high salinity, except for sodium errors at $pH > 10$ that can be reduced by using a "low sodium error" electrode.
- 5.2 Coatings of oily material or particulate matter can lessen electrode response. Remove these coating wiping gently or washing with detergent, followed by distilled water rinsing. An additional treatment with HCl (1:9) may be necessary to remove any remaining film.

- 5.3 pH measurements are affected by temperature in two ways. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instrument having temperature compensation or by calibration the electrode-instrument system at samples temperatures. This error is sample dependent and cannot be controlled, therefore, both the pH and the temperature should be reported at the time of analysis.

6.0 Safety

- 6.1 The toxicity or carcinogenicity of each analyte, compound, or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in these analyses.
- 6.2 Follow the GLP procedures, read MSDS and labels for each reagent used.

7.0 Equipment and Supplies

- 7.1 pH meter - laboratory or field model.
7.2 Combination electrode.
7.3 Automatic temperature compensation probe.
7.4 Magnetic stirrer and teflon-coated stirring bar.
7.5 Beakers: 100 ml.

8.0 Reagents and Standards

- 8.1 Reagent Water. The Laboratory Water System consist of reverse osmosis followed by cation and anion exchange resins, activated carbon and a 0.2 μ m final filter.
- 8.2 Buffer solutions of known pH: 4.00, 7.00 and 10.00. Available commercially.

9.0 Sample Collection, Preservation, Shipment and Handling

- 9.1 Sample should be analyzed as soon as possible preferably in the field at the time of sampling.
- 9.2 High-purity waters and wastes not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore, the sample containers should be filled completely and kept sealed prior to analysis.

10.0 Quality Assurance/Quality Control

- 10.1 All quality control data should be available for reference or inspection.
- 10.2 Run a duplicate sample every batch.

- 10.3 Quality control sample (QCS)- when beginning the use of the method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analysis of a QCS. If the determined concentrations are within $\pm 10\%$ of the stated values, performance is unacceptable. Identify and correct the source of the problem.
- 10.4 Precision and bias:
- 10.4.1 A precision of ± 0.02 pH units and an accuracy of ± 0.05 pH units can be achieved.
- 10.4.2 ± 0.1 pH unit represents the limit of accuracy under normal conditions, especially for measurement of water and poorly buffered solutions.
- 10.5 The laboratory shall maintain records to define the quality of data that is generated.
- 10.6 Use fresh buffer solution daily for best accuracy.
- 10.7 Keep buffers solutions well stoppered and replace at a shelf age of 3 months, or sooner if visible change is observed; always keeping in mind solution's expiration date.

11.0 Calibration and Standardization

- 11.1 The instrument is calibrated at least once a day to ensure an acceptable operation of the meter or every time the instrument is turn ON.
- 11.2 The instrument daily calibration is logged on the current pH analysis logbook.
- 11.3 Use fresh buffer solution (4.00, 7.00, 10.00) daily for best accuracy.
- 11.4 Calibrate first with the buffer solution of 7.00.
- 11.5 See Section 14.0 for calibration of Orion 4 Star pH/ ISE Benchtop meter in pH mode.

12.0 Sample Preparation (Procedure)

- 12.1 For the standardization of the pH meter and electrode system see Section 14.0 of the SOP. The purpose of standardization is to adjust the response of the glass electrode to the instrument.
- 12.2 Place the sample in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give an adequate clearance for the magnetic stirring bar. The purpose of stirring is to insure homogeneity; stir gently to minimize carbon dioxide entrainment.
- 12.3 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movements across the electrode sensing element as indicated by drift free (<0.1 pH) readings.

- 12.4 Rinse electrode and wipe gently, immerse into the sample beaker or sample stream and stir at a constant rate. Rate of stirring should minimize the air transfer rate at the air water interface of the sample.
- 12.5 Record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

13.0 Quantitative Determination (Calculations)

- 13.1 The result of pH is read direct from the instrument in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest 0.1°C.

14.0 Instrument Performance

- 14.1 Calibration of Orion 4 Star pH/ ISE Benchtop meter in pH mode
 - 14.1.1 The instrument is calibrated at least once a day to ensure an acceptable operation of the meter or every time the instrument is turn ON.
 - 14.1.2 The instrument daily calibration as logged on the current pH analysis logbook.
 - 14.1.3 Press the ON key to turn on the instrument.
 - 14.1.4 Submerge the pH electrode and the temperature compensation probe in a buffer 7.00 solution.
 - 14.1.5 Press the calibration key.
 - 14.1.6 The pH CAL message will be displayed momentarily on the instrument.
 - 14.1.7 The CAL 1 message will remain on the bottom of the screen.
 - 14.1.8 The pH icon located at the right of the screen will scintillate until the mv is stable.
 - 14.1.9 The left arrow icon located at the left of the screen will scintillate, when stable; while the pH icon will stop blinking.
 - 14.1.10 Log the pH and temperature displayed on the current pH analysis logbook. Also, log the buffer lot number and its expiration date.
 - 14.1.11 Press the calibration key again.
 - 14.1.12 The CAL 2 message will be displayed at the bottom of the screen.
 - 14.1.13 Remove the pH electrode and the temperature compensation probe from the buffer solution and thoroughly clean them with distilled water. Dry with a lint free wipe after wash.
 - 14.1.14 Submerge the probes on the next buffer used for calibration (i.e. 4.00 or 10.00 SU).
 - 14.1.15 The pH icon located at the right of the screen will scintillate until the mv is stable.
 - 14.1.16 The left arrow icon located at the left of the screen will scintillate, when stable; while the pH icon will stop blinking.
 - 14.1.17 Log the pH and temperature displayed on the current pH analysis logbook. Also, log the buffer lot number and its expiration date.
 - 14.1.18 Press the calibration key again.
 - 14.1.19 The CAL 3 message will be displayed at the bottom of the screen.
 - 14.1.20 Repeat steps 13 to 19 with a third buffer. When finished, and the CAL 4 message is displayed at the bottom of the screen, press the measure, save/print key.
 - 14.1.21 The slope will be displayed momentarily.

- 14.1.22 Log the slope on the current pH analysis logbook.
14.1.23 The meter is ready to be used for pH measurements.

15.0 Pollution Prevention

- 15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be reduced feasibly at the source, the Agency recommends recycling as the next best option. The acids used in this Method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this Method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.
- 15.2 For information about pollution prevention that may be applied to laboratories and research institutions, consult "*Less is Better: Laboratory Chemical Management for Waste Reduction*", available from the American Chemical Society's Department of Governmental Relations and Science Policy, 115 16th Street NW, Washington DC 20036, (202)872-4477.

16.0 Data assessment and acceptance criteria for quality control measures

- 16.1 Procedure is available at Beckton Quality Manual.

17.0 Corrective Actions for Out-of-Control data.

- 17.1 The procedure is available at Beckton Quality Manual.

18.0 Contingencies or handling-of-Control or unacceptable data.

- 18.1 The procedure is available at Beckton Quality Manual.

19.0 Waste Management

- 19.1 It is the laboratory's responsibility to comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land-disposal restrictions. In addition, it is the laboratory's responsibility to protect air, water, and land resources by minimizing and controlling all releases from fume hoods and bench

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operations. Also, compliance is required with any sewage discharge permits and regulations.

- 19.2 Samples containing acids at a pH of less than 2 are hazardous and must be neutralized before being poured down a drain or must be handled as hazardous waste.
- 19.3 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 115 16th Street NW, Washington, DC 20036.

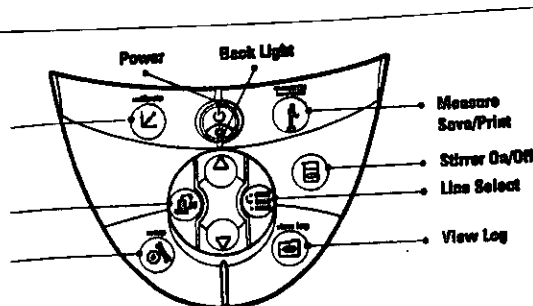
20.0 References

- 20.1 Standard Method for the Analysis of Wastes and Wastewaters, 19th, 1995 SM 4500-H⁺B.
- 20.2 "OSHA Safety and Health Standards, General Industry," 29 CFR 1910, OSHA 2206 (1976).
- 20.3 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety (1979).
- 20.4 "Method of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL Cincinnati, OH 45268, EPA-4-79-019 (March, 1979).

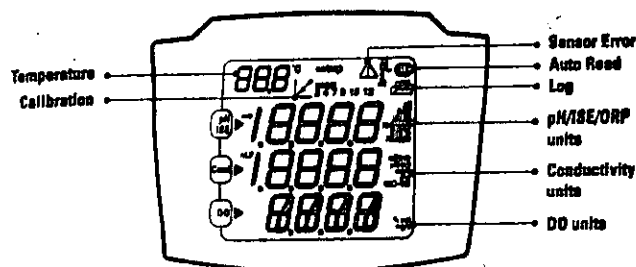
21.0 Tables, Diagrams and/ or Flowcharts

21.1 Diagram of Orion 4 Star Benchtop pH/ISE

21.1.1 Keypads functions



21.1.2 Display Overview



HISTORY OF REVISIONS			
REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
3	Sept /98	pag 4 Part II	calibrate ph meter starting w/ pH 7.00 select a second buffer that brackets the sample with pH 7.00 buffer.
—	—	—	use each aliquot of buffer once, and discard after calibration is done.
4	Nov/98	pag 7 Sec. 14	Efficiency Factor range 0.95 to 1.05
5	Sept/99	NONE	SOP's cover added.
6	Dec/00	—	revised Secs. as per helac audit.
7	April/02	pag 6,7	as per EPA audit 7/01
8	June/03	pag 1	(pH 150.1) Test Method I.D.
9	6/06	1—	(Orian 4-111) new ph meter, procedure
10	6/07	NONE	No change
11	9/08	none	Gembor Formata SOP
12	4/09	none	Revised SOP